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GAYE TURNER
TEAM LEADER EXAMINATION
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AUSTRALIA

Patents Act 1990

Provisional Specification

for invention entitled:

INFRARED INK COMPOSITION (INK02)

The invention is described in the following statement: -

FIELD OF THE INVENTION

The present invention relates to compounds that are suitable for use as dyes. In particular, the present invention relates to compounds that are suitable for use as infrared dyes, to compositions containing these
5 compounds, including colour light-sensitive material, and to processes for their use as infrared absorbers. The present invention has particular application to infrared printing inks.

BACKGROUND

Recently there has been renewed interest in "innovative" or "functional"
10 dyes. One area of interest is that of optical recording technology where gallium aluminium arsenide (GaAlAs) and indium phosphide (InP) diode lasers are widely used as a light source. Since dyes absorbing in the near infrared (near-IR) region (i.e., beyond about 700 nanometers in wavelength and less than about 2000 nanometers in wavelength are required and the oscillation
15 wavelengths fall in the near-infrared region, they are suitable candidates for use as infrared dyes.

Infrared dyes have applications in many areas. For example, infrared dyes are important in the optical data storage field, particular in the DRAW (Direct Reading After Writing) and WORM (Write Once, Read Many) disk,
20 which is used for recording. Currently, indolinocyanine dyes, triphenylmethane dyes, naphthalocyanine dyes and indonaphthalometal complex dyes are commercially available for use as organic colorants in DRAW disks. Cyanine dyes can only be used if additives improve the lightfastness.

25 Another application of infrared dyes is in thermal writing displays. In this application, heat is provided by a laser beam or heat impulse current. The most common type of infrared dyes used in this application are the cyanine dyes, which are known as laser dyes for infrared lasing.

Infrared dyes are also used as photoreceptors in laser printing. Some
30 infrared-absorbing dyes are used in laser filters. They also find application in infrared photography and even have application in medicine, for example, in photodynamic therapy.

The compounds of the present invention will now be described in the context of printing inks and the like, but it will be understood by the skilled
35 reader that the compounds described hereunder may be used in other applications, for example, those set out above.

Fast, error-free data entry is important in current communication technology. Automatic reading of digital information in printed, digital and analog form is particularly important. An example of this technology is the use of printed bar codes that are scannable. In many applications of this technology, the bar codes are printed with inks that are visible to the unaided eye. There are, however, applications (e.g. security coding) that require the barcode or other intelligible marking to be printed with an ink that invisible to the unaided eye but which can be detected under UV light or infrared light (IR).

For instance, U.S. Pat. No. 5,093,147 describes a method exploiting the process of fluorescence in which a dye is excited by ultra-violet (UV), visible or near-IR radiation and fluorescent light emitted by the dye material is detected. This reference describes a jet printing process used to apply a compatible liquid or viscous substance containing an organic laser dye that is poorly absorptive of radiation in the visible wavelength range of about 400 nm to about 700 nm, and is highly absorptive of radiation in the near-IR wavelength range of about 750 nm to about 900 nm. The dye fluoresces at longer wavelengths in the IR in response to radiation excitation in the near-IR range.

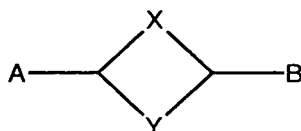
Another example is described in U.S. Pat. No. 5,460,646 (Lazzouni et al) which describes the use of a colorant which is silicon (IV) 2,3-naphthalocyanine bis((R₁)(R₂)(R₃)-silyloxy) wherein R₁, R₂, and R₃ are selected from the group consisting of an alkyl group, at least one aliphatic cyclic ring, and at least one aromatic ring.

The infrared absorbing dyes Squarylium and Croconium dyes have been extensively described in the literature (see for example, T. P. Simard, J. H. Yu, J. M. Zebrowski-Young, N. F. Haley and M. R. Detty, *J. Org. Chem.* **65** 2236 (2000), and J. Fabian, *Chem. Rev.* **92** 1197 (1992)). These prior art compounds have a central squarylium or croconium moiety connected to traditional electron donors. However, these particular dyes do not absorb at a high enough wavelength and/or also absorb too strongly in the visible spectrum.

DISCLOSURE OF THE INVENTION

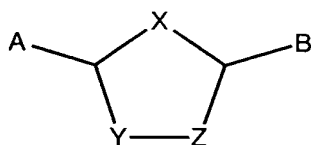
We have identified compounds that may be suitable for use as infrared dyes.

Accordingly, the present invention provides, in one aspect, infrared dyes of the following formulae:



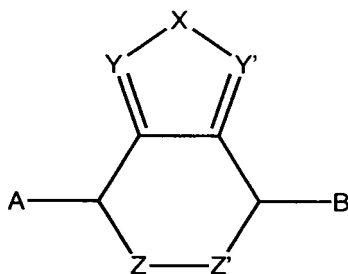
1

wherein, X is CO and Y is selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Y are independently selected from the group consisting of O, S, Se, CS, Te, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



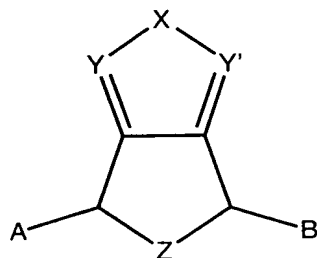
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wherein X is CO and Y and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein Y and Z are each CO and X is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Z are each CO and Y is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Y are each CO and Z is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X, Y and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



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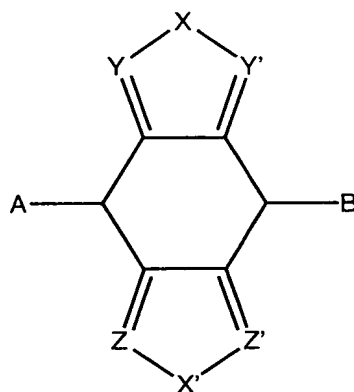
wherein X and Z and Z' are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y and Y' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



4

5

wherein X and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y and Y' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



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wherein X and X' are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y, Y', Z and Z' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;

15

and wherein R is the group consisting of hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted thioalkyl group

and wherein -A and -B in Formulae 1 to 5 given above are independently selected from moieties containing $2n$ carbon atoms each of which are connected to three (3) atoms at least one (1) of which is one (1) of the $2n$ carbon atoms other than a carbon atom that is double bonded to a heteroatom, wherein n is an integer equal to or greater than 1.

In regard to -A and -B, for example in compound 50 the carbon atom having a double bond to the oxygen (heteroatom) is not counted as one of the carbon atoms and therefore in this case $2n = 6$ and in the case of 53, $2n = 10$

Preferably -A and -B are the same.

The terminal group of -A and/or -B may or may not form part of a ring structure.

The infrared dyes of the present invention may be poorly absorptive of light in the visible range of about 400 to 700 nanometers but highly absorptive in the near infrared range of wavelengths of at least 700 nanometers.

In a further aspect, the present invention provides a composition of matter including a dye in accordance with the first aspect of the invention.

In yet a further aspect, the present invention provides a method for using a dye in accordance with the first aspect

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A to 1C: show a calculated absorption spectra for Formula 1 dyes;

Figures 2A to 2C: show calculated absorption spectra for Formula 2 dyes.

Figure 3: shows calculated absorption spectra for Formula 3 dyes.

Figure 4: shows calculated absorption spectra for Formula 4 dyes.

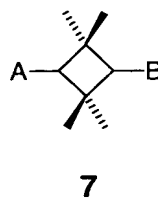
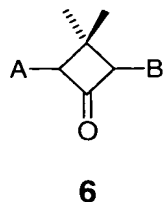
Figures 5A and 5B: show calculated absorption spectra for Formula 5 dyes.

Figures 6A to 6E: show calculated absorption spectra for Formula 1 dyes as function of -A and -B that are the same as each other.

Figures 7A to 7F: show calculated absorption spectra for Formula 2 dyes as function of -A and -B that are the same as each other.

EMBODIMENTS

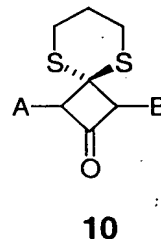
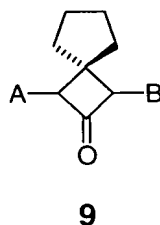
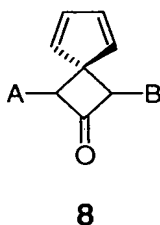
SYNTHESIS OF COMPOUNDS OF FORMULA 1



The calculated absorption spectra for compounds **6** and **7** of Formula **1** are shown in Figure 1.

From Squarylium Dyes

Compounds according to Formula **1** are similar to the squarylium dyes. However, one, or in the case of molecule **6**, two carbonyl groups are reduced. The synthesis of such molecules may start from the squarylium dyes. Several methods are known whereby two hydrogens replace the oxygen of an aldehyde or ketone; this process is known as deoxygenation. One such method is the Wolff-Kishner reduction. The first step in the reaction sequence is the formation of the hydrazone by addition of hydrazine and elimination of water. Base attacks the somewhat acidic NH_2 group to form an ambident anion that can react with a proton donor to produce a diazene $\text{R}_2\text{CH-N}=\text{NH}$. The acidic diazene ($\text{pK}_a \approx 23$) reacts with base forming an anion that loses nitrogen to give the hydrocarbon. The reaction is normally carried out by heating the ketone with hydrazine hydrate and sodium hydroxide in diethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, which has a B/P. of 245°C . Alternatively, the reduction may be carried out in the polar aprotic solvent DMSO at 100°C . The hydrazone forms, and water distills out of the mixture. On refluxing, nitrogen is evolved, and the product is isolated. The end product can be reacted with methyl iodide with a strong base to give the methylated species.



An alternative procedure for the direct reduction of a carbonyl group to a methylene group involves refluxing the aldehyde or ketone with amalgamated zinc and hydrochloric acid (Clemmensen reduction [2]).

- 5 Amalgamated zinc is zinc with a surface layer of mercury. It is prepared by treating zinc with an aqueous solution of a mercuric salt. Since zinc is higher on the electromotive force scale than mercury, it reduces mercuric ions to mercury. The reduction of the carbonyl compound occurs on the surface of the zinc, and, like many heterogeneous reactions, this reaction does not have a
10 simple mechanism. The Clemmensen reduction is suitable for compounds that can withstand treatment with hot acid. Many ketones are reduced in satisfactory yields.

From Cyclobutanone

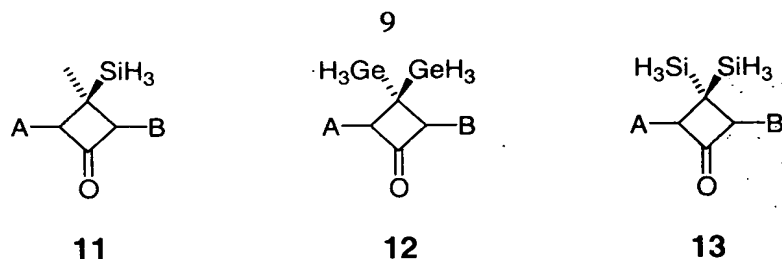
- 15 The acidity of hydrogen adjacent to carbonyl groups can be utilized by reacting cyclobutanone with a protected alanine in the presence of a base. A good nucleofugic leaving group at the *para* position of the alanine is needed to ensure that a non-negligible yield is obtained. The product can be reacted with excess methyl iodide with a strong base to give the methylated species.

- 20 The sulfur equivalent of Molecules **6** and **7** were found to have large absorption peaks in the visible part of the spectrum.

- Ring closure methods may be used to synthesize Molecules **8** and **9**. This could be achieved by using, for example, a 1,2-ethyl dihalide instead of a methyl halide in the final reaction step for the formation of Molecule **6** above.
25 Different stages of dehydrogenation will give either Molecule **8** or Molecule **9**.

An alternative method could be to begin with the oxygenation of spiro[3,4]octa-5,7-diene (CAS No: 15439-15-3) at the 2 position. The adjacent acidic hydrogens can then participate in substitution reactions with A and B. Dehydrogenation then gives the products of Molecules **8** and **9**.

- 30 The addition of 1,3-propanedithiol to a squarylium dye under the conditions of an acid catalysis will react with a carbonyl group to give the cyclic thioacetal of Molecule **10**.



The calculated absorption spectra for compounds **8**, **9** and **10** are shown in Figure 1B.

The use of other group 4 elements instead of carbon in the formation of Molecule **6** leads to a significant bathochromic shift. However, the absorption peaks in the UV have also been shifted into the red part of the spectrum. Germanium would give an orangish dye and silicon would give a pale yellow dye. Molecule **11** combines both carbon and silicon that does not absorb as far in the infrared as Molecules **12** and **13**. However, the infrared peak has been shifted approximately 160nm bathochromically with respect to the squarylium dye while keeping the absorption intensity in the visible spectrum to a relatively low level.

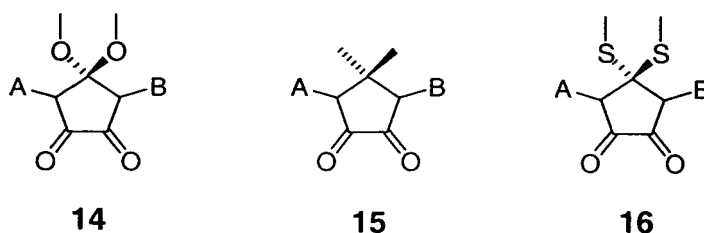
The calculated absorption spectra for compounds **11**, **12** and **13** are shown in Figure 1C.

Synthesis of compounds of Formula 2

From Croconium Dyes

The more reactive of the carbonyl groups can be converted to acetal or thioacetals. When the ketone is treated with an alcohol and an acid catalyst **14** is formed. However, with ketones, the equilibrium constant for acetal formation is generally unfavorable. For this reason the reaction is usually carried out with the alcohol as solvent in order to drive the equilibrium to the acetals. The acetals are generally stable to basic conditions.

Desulfurization of thioacetals provides a method for net deoxygenation of aldehydes and ketones and is complementary to the Wolff-Kishner and Clemmensen deoxygenations. Methyl sulfide reacts with the ketone under conditions of acid catalysis (BF_3) to give the thioacetal shown as **16** of Formula 2. Acetals and thioacetals are commonly used as protective groups for carbonyls [3].



Molecule **15** may be produced by the same method as the four member analogues.

The calculated absorption spectra for compounds **14**, **15** and **16** of Formula **2** are shown in Figure 2A.

From Cyclopentene

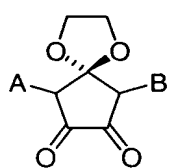
A possible alternative method could be to use a derivative of 4-cyclopentene-1, 3-dione (CAS No: 930 60-9) which is very similar to croconic acid. The acidic hydrogens of the beta-diketones can readily react with methyl iodide to give the methylated species. For example: 1 equivalent of NaOH, methyl iodide and water will give 4-cyclopentene-2-methyl-1, 3-dione. Two equivalents of NaOMe with methyl iodide and methanol will give the di-methyl derivative. Substitution of hydroxy groups for hydrogen in the 4 and 5 positions will enable the product to react with R in a similar process to croconium dyes. This could produce the dyes shown as molecule **15**. Different functional groups, instead of the methyl groups at the 2 position could also be used.

From Cyclic α -Diketone

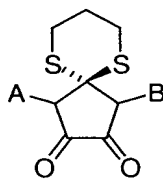
α -Diketones may be obtained by the mild oxidation of α -hydroxy ketones that are available by the acyloin condensation [4]. α -Diketones is also available by the direct oxidation of simple ketones with selenium dioxide [5]. The adjacent acidic hydrogens to the carbonyl groups will enable aniline to react with the α -Diketone in a basic solution [6]. A substitution reaction using a strong base and, for example methanol may give **14**.

The addition of 1,2-ethanediol and 1,3-propanedithiol, as with Formula **1** molecules, to the croconium dyes under the conditions of an acid catalysis gives the cyclic acetal (**17**) and the thioacetal (**18**).

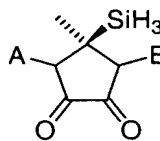
The use of silicon again shifts the absorption peak significantly to longer wavelengths. However, appreciable absorption is now occurring in the visible spectrum giving the dye an orange color.



17



18

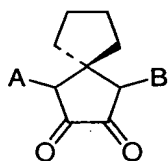


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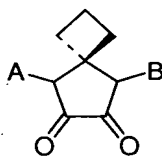
The calculated absorption spectra for compounds **17**, **18** and **19** are shown in Figure 2B.

As for compounds of Formula **1**, ring closure may be performed on the beta carbon of the 1-diketones. Alternatively, functionalization of the spiro compounds, such as spiro[4,4]nona-1,3-diene (CAS No: 766-29-0), could lead to **20**. The corresponding compounds for **21** and **22** are spiro[3,4]octa-5,7-diene (CAS No: 15439-15-3) and spiro[2,4]hepta-4,6-diene (CAS No: 765-46-8) respectively.

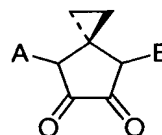
Reaction with the side group -A and -B may give **22** and water. This and larger spiro compounds could then be reacted with the appropriate -A and -B to form the dyes shown as Molecules **20**, **21** and **22**. The calculated absorption spectra for compounds **20**, **21** and **22** are shown in Figure 2C. A pattern is seen where an increase in size of the spiro compound results in a lower value of the absorption maximum. This also shifts the peak in the blue part of the visible spectrum down into the ultra-violet wavelengths.



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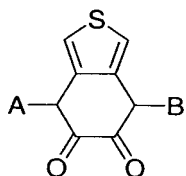
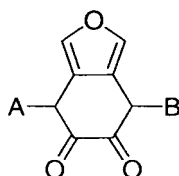
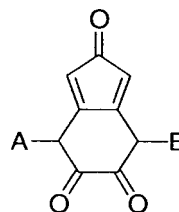


22

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Substitution of silicon for the central spiro carbon atom was found to decrease the maximum absorption wavelength.

COMPOUNDS OF FORMULA 3

**23****24****25**

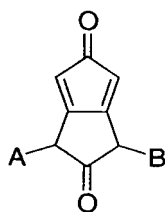
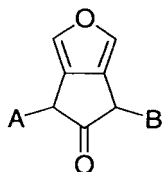
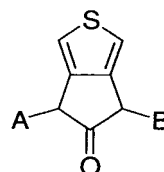
The calculated absorption spectra for compounds **23**, **24** and **25** shown
 5 above of Formula 3 are shown in Figure 3A.

A possible method of synthesis is to start with a thiophene, furan and
 2,4-Cyclopentadiene-1-one (CAS No: 13177-38-3) respectively to give **23**, **24**
 and **25** respectively. However, as the C2 and C5 positions need to be blocked
 in order to functionalize the C3 and C4 positions it is doubtful that ring
 10 closure could be achieved readily.

A more preferred method of synthesis is to begin with *p*-quinone.
 Addition of aldehydes to the C2 and C3 positions could give ring closure to
 give the thiophene and their analogues by standard techniques.

15 COMPOUNDS OF FORMULA 4

Examples of compounds of Formula 4 are compounds **26**, **27** and **28**
 shown below. The calculated absorption spectra for compounds **26**, **27** and
28 are shown in Figure 4.

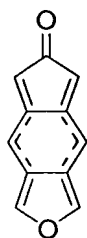
**26****27****28**

20

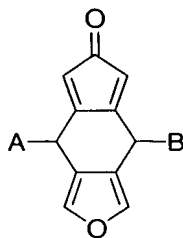
COMPOUNDS OF FORMULA 5

Examples of compounds of Formula 5 are compounds **29**, **30**, **31** and
32 shown below. The calculated absorption spectra for compounds **29** - **32**
 are shown in Figure 5A and 5B respectively (R = *N*-dialkyl aniline).

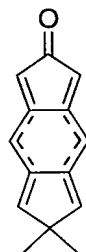
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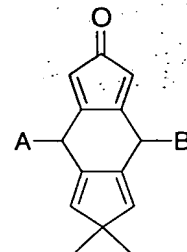
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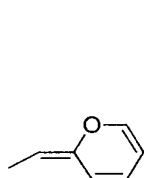


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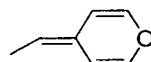
**The effect of the R moiety on the absorption spectra of
Formula 1 compounds**

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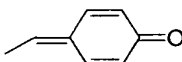
The calculated absorption spectra of compounds having $-A (= -B)$ groups **33** to **45** shown below is presented in Figures 6A to 6E respectively.



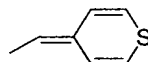
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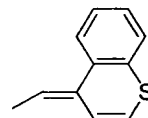
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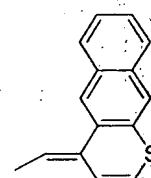
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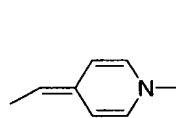
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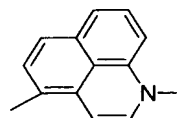
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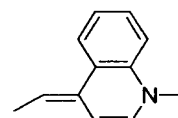
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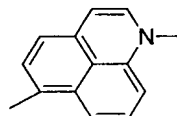
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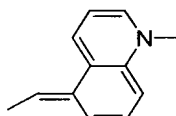
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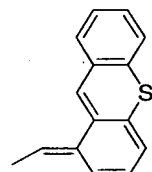
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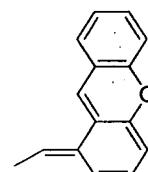
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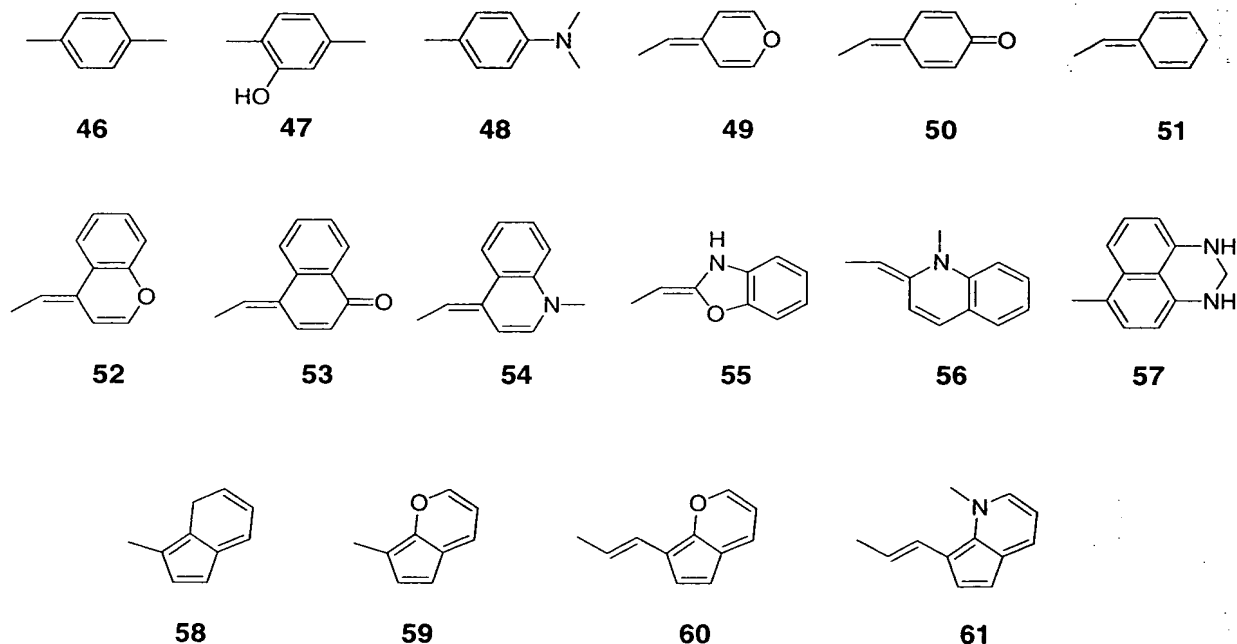


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**The effect of the $-A (= -B)$ moiety on the absorption spectra of
Formula 2 compounds**

The calculated absorption spectra of compounds having $-A (= -B)$ groups **46** to **61** shown below is presented in Figures 7A to 7H respectively.



Throughout this specification the word "comprise", or variations such
 5 as "comprises" or "comprising", will be understood to imply the inclusion of a
 stated element, integer or step, or group of elements, integers or steps, but not
 the exclusion of any other element, integer or step, or group of elements,
 integers or steps.

10 It will be appreciated by persons skilled in the art that numerous
 variations and/or modifications may be made to the invention as shown in the
 specific embodiments without departing from the spirit or scope of the
 invention as broadly described. The present embodiments are, therefore, to
 be considered in all respects as illustrative and not restrictive.

Dated this fourteenth day of August 2000

Silverbrook Research Pty Ltd

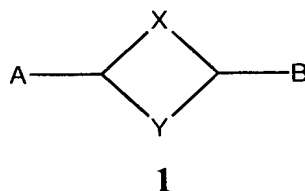
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References

- 1: J. Fabian, *Chem. Rev.*, 92, 1197, (1992).
- 5 2: *Journal of Organic Chemistry*: 35, 532 (1970); 38, 1735, 1738, 2747 (1973); 40, 271, 3306 (1975); 41, 1494, 3465 (1976); 46, 4139, 5060 (1981); 48, 254 (1983); 50, 5727 (1985), *Journal of the Chemical Society: Chemical Communications*: 595 (1972); 237 (1981), *Organic Syntheses* 55 7 (1976), *Tetrahedron Letters* 27 1719, 1723 (1986)
- 10 3: Philip J. Kocienski, *Protecting Groups*, Georg Thieme Verlag Stuttgart, New York, NY (USA), (1994).
- 4: A. Streitwieser, C. H. Heathcock and W. M. Kosower, *Introduction To Organic Chemistry* 4th Ed. p866, Macmillan, New York (1992).
- 15 5: A. Streitwieser, C. H. Heathcock and W. M. Kosower, *Introduction To Organic Chemistry* 4th Ed. p884, Macmillan, New York (1992)
- 20 6: M. Sainsbury, *Aromatic Chemistry*, Oxford University Press, New York p51 (1992).

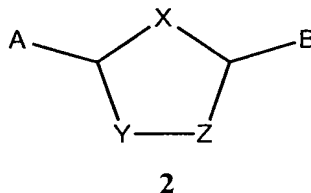
CLAIMS:

1. An infrared dye according to one of the following formulae:



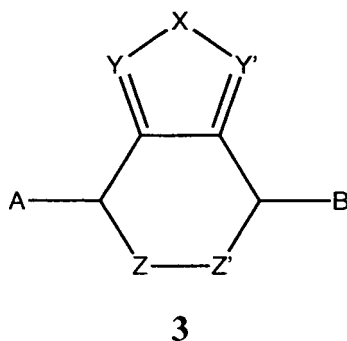
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- wherein, X is CO and Y is selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Y are independently selected from the group consisting of O, S, Se, CS, Te, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



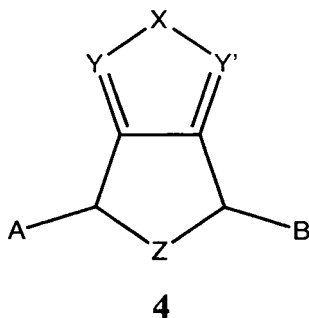
- wherein X is CO and Y and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein Y and Z are each CO and X is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Z are each CO and Y is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X and Y are each CO and Z is selected from the group O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; or wherein X, Y and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;

25



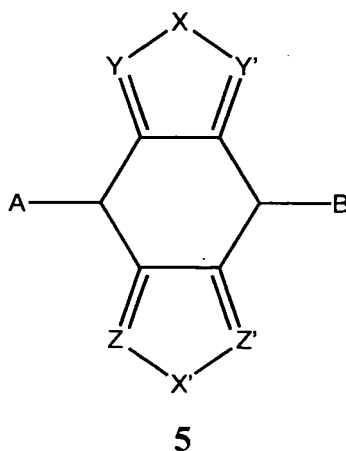
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wherein X and Z and Z' are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y and Y' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



10

wherein X and Z are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y and Y' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which may be the same or different, are selected from the group R;



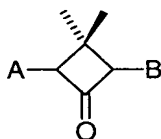
wherein X and X' are independently selected from the group consisting of O, S, Se, Te, CS, CR₁R₂, NR₁, SiR₁R₂, GeR₁R₂, PR₁, R'; Y, Y', Z and Z' are independently selected from the group CR₁, N; and wherein R₁ and R₂, which
 5 may be the same or different, are selected from the group R;

and wherein R is the group consisting of hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted
 10 alkoxy group, a substituted or unsubstituted thioalkyl group

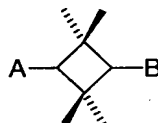
and wherein -A and -B in Formulae 1 to 5 given above are independently selected from moieties containing 2n carbon atoms each of which are connected to three (3) atoms at least one (1) of which is one (1) of the 2n carbon atoms other than a carbon atom that is double bonded to a
 15 heteroatom, wherein n is an integer equal to or greater than 1.

2. An infrared dye according to claim 1 wherein the dye is of Formula 1.

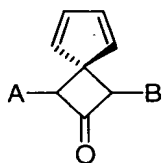
3. An infrared compound according to claim 2 having the formula selected
 20 from the group consisting of:



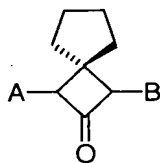
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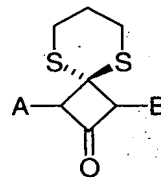
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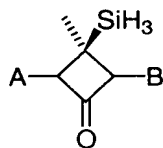
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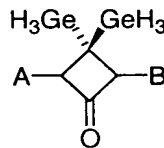
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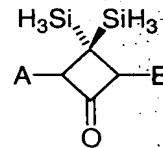
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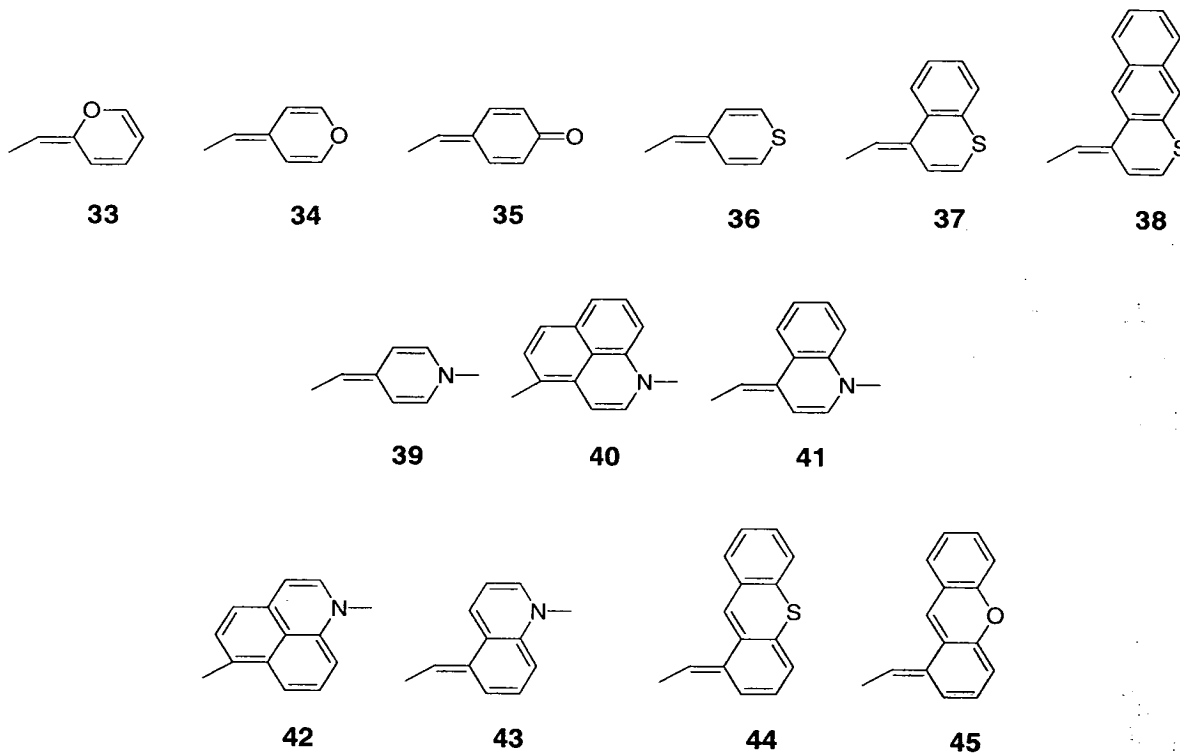


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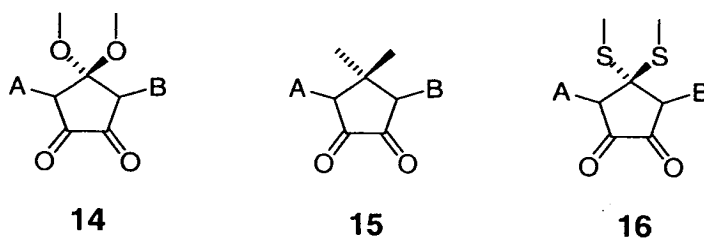


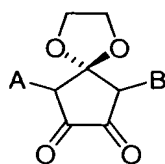
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- 5 3. An infrared dye according to claim 1 or claim 2 wherein -A and -B are each independently selected from the group consisting of:

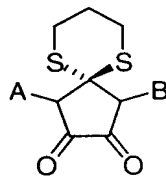


4. A compound according to claim 2 wherein -A and -B are the same.
- 10 5. A compound according to claim 1 of Formula 2.
6. A compound of claim 5 having a formula selected from the group consisting of:

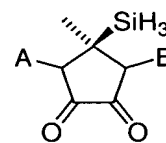




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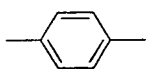
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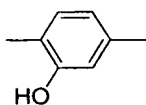
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7. A compound according to claim 5 or claim 6 wherein -A and -B are each independently selected from the group consisting of:

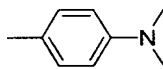
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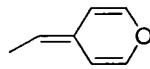
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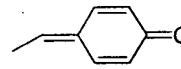
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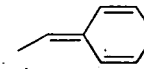
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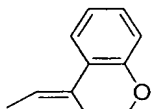
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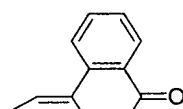
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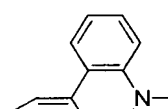
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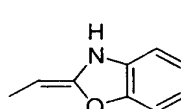
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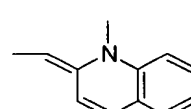
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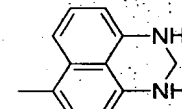
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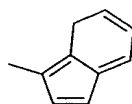
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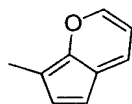
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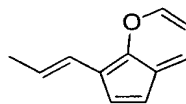
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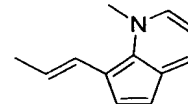
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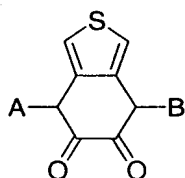


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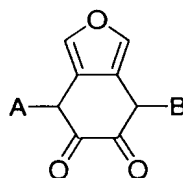
8. A compound of claim 1 of Formula 3.

9. A compound of claim 8 having a formula selected from the group consisting of:

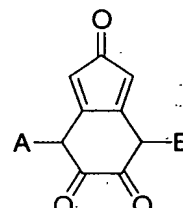
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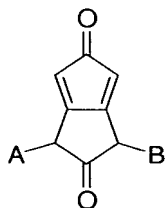
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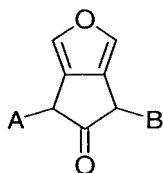
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10. A compound of claim 1 of Formula 4.

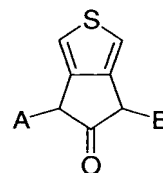
11. A compound of claim 10 having a formula selected from the group
5 consisting of:



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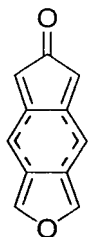
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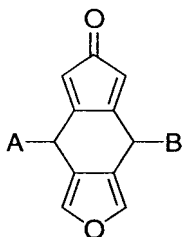
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12. A composition of claim 1 of Formula 5.

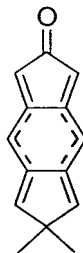
10 13. A compound of claim 12 having a formula selected from the group
consisting of:



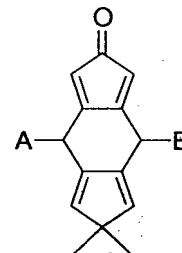
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14. An infrared dye composition comprising a compound according to
claim 1.

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15. A solvent-based ink composition comprising a compound according to
claim 1.

16. A solvent-based ink according to claim 15 which is ink jet printer ink.

20

ABSTRACT

An infrared dye, characterised in that the dye comprises of Formulae 1 to 5

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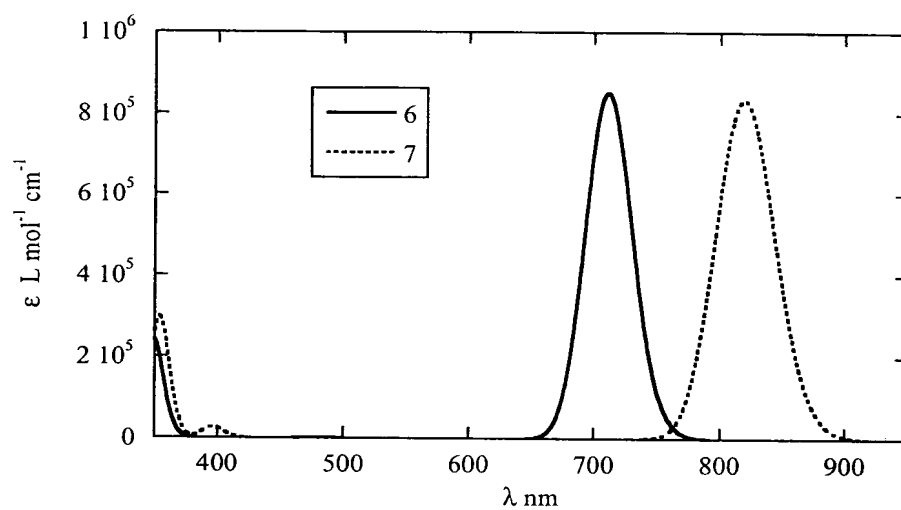


Figure 1A: Calculated absorption spectra for Formula I dyes.

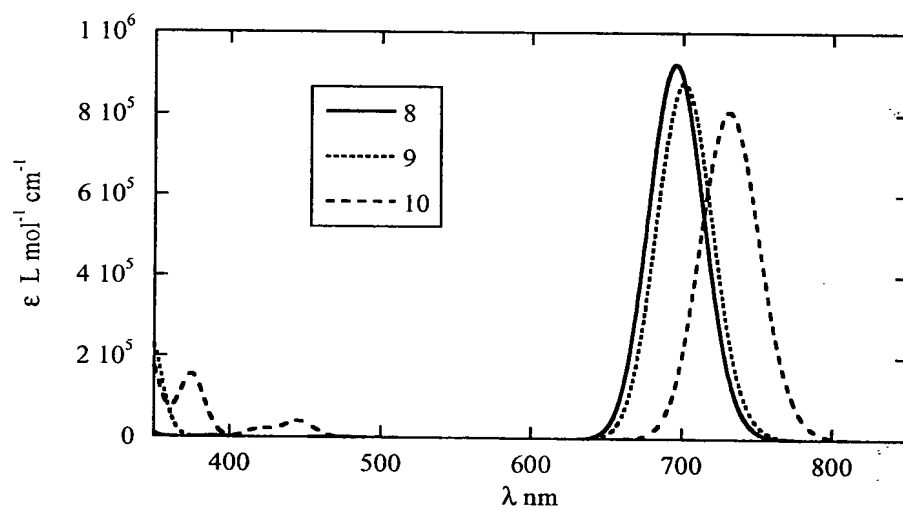


Figure 1B: Calculated absorption spectra for Formula I dyes.

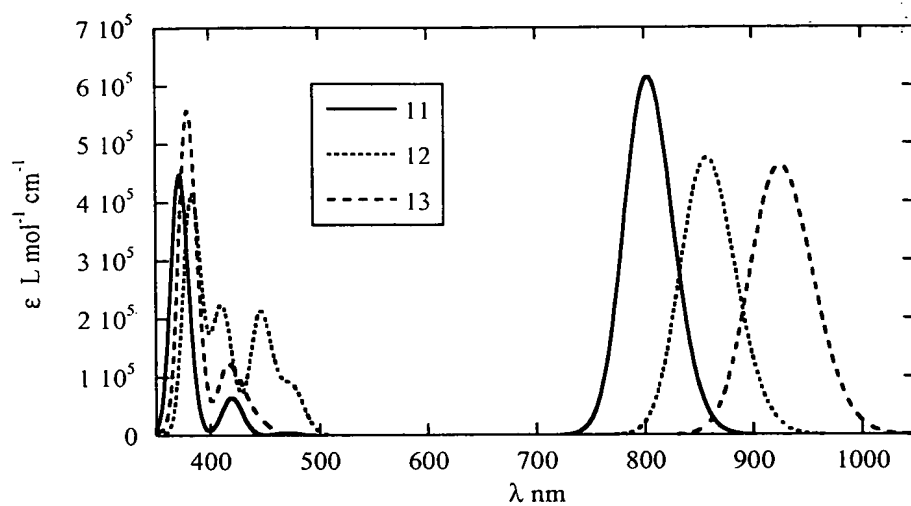


Figure 1C: Calculated absorption spectra for Formula I dyes.

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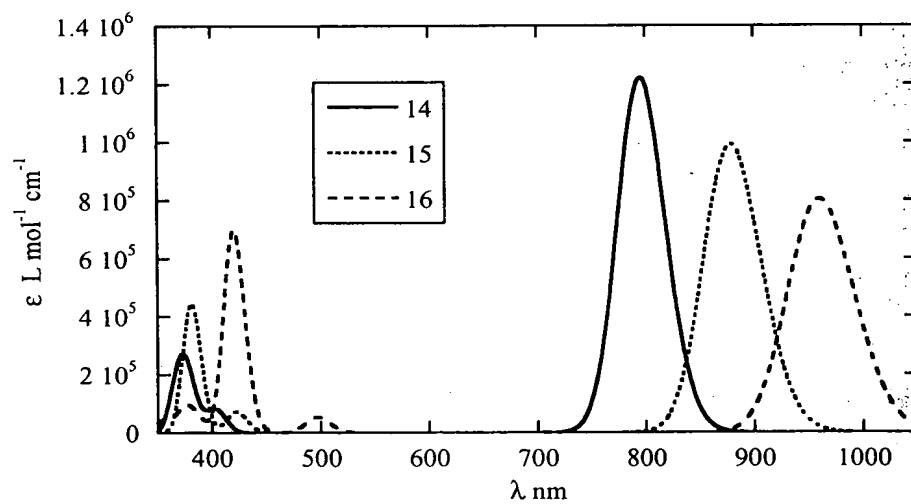


Figure 2A: Calculated absorption spectra for Formula II dyes.

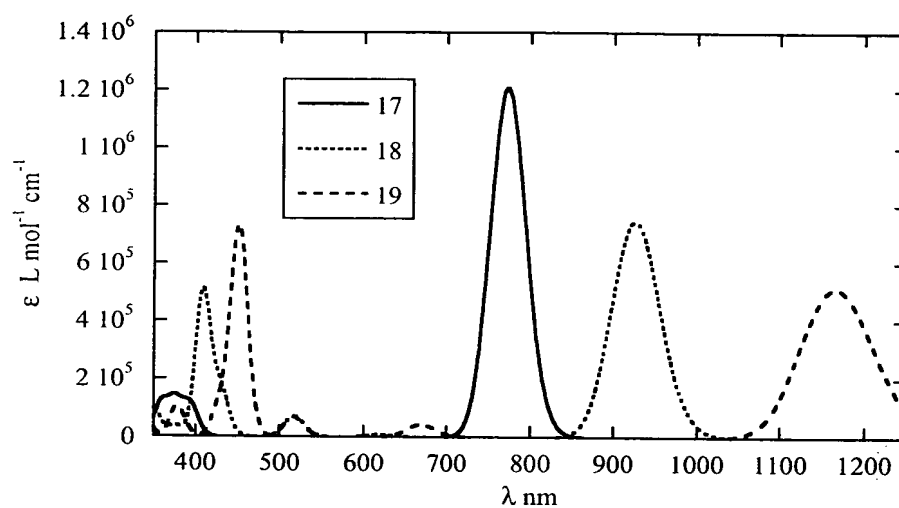
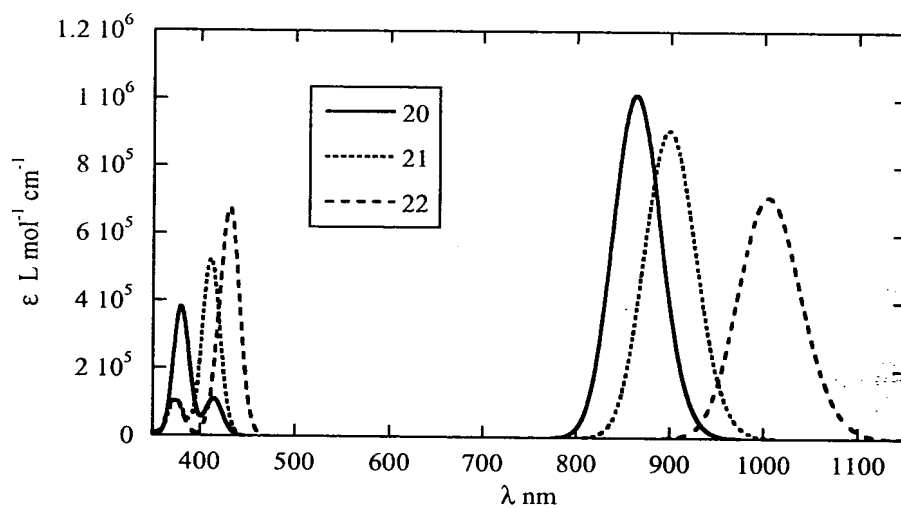


Figure 2B: Calculated absorption spectra for Formula 2 dyes.



5 Figure 2C: Calculated absorption spectra for Formula 2 dyes.

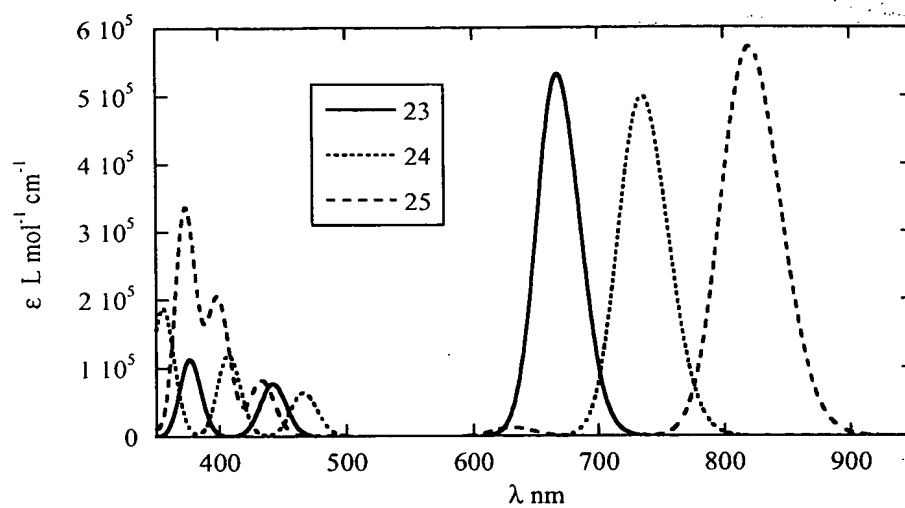


Figure 3: Calculated absorption spectra for Formula 3 dyes.

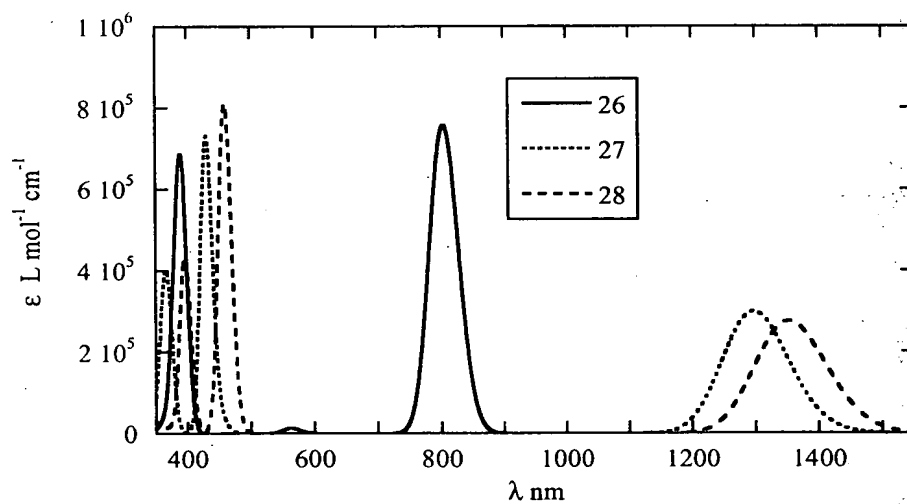


Figure 4: Calculated absorption spectra for Formula 4.

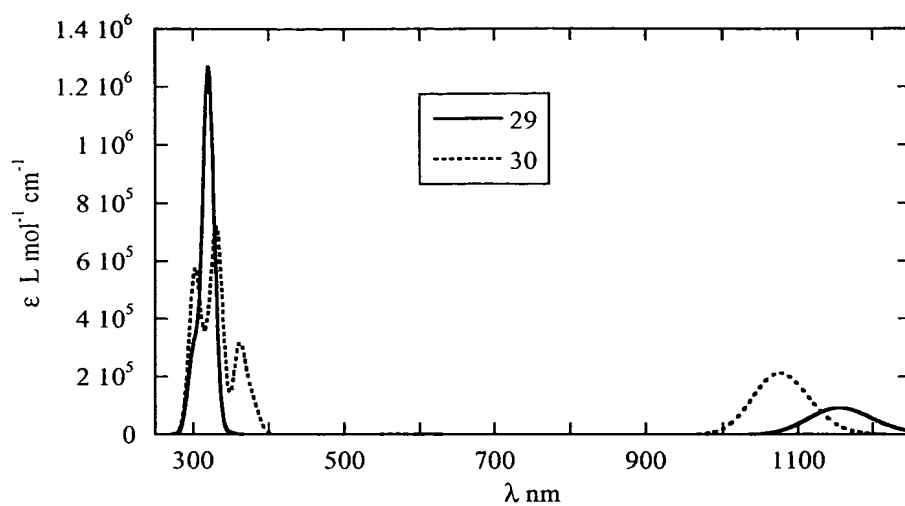
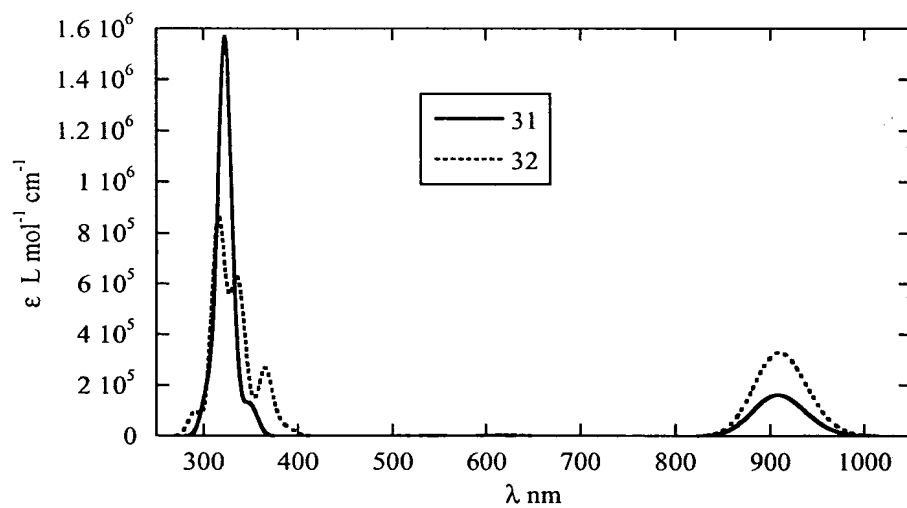


Figure 5A: Calculated absorption spectra for Formula 5.



5 Figure 5B: Calculated absorption spectra for Formula 5.

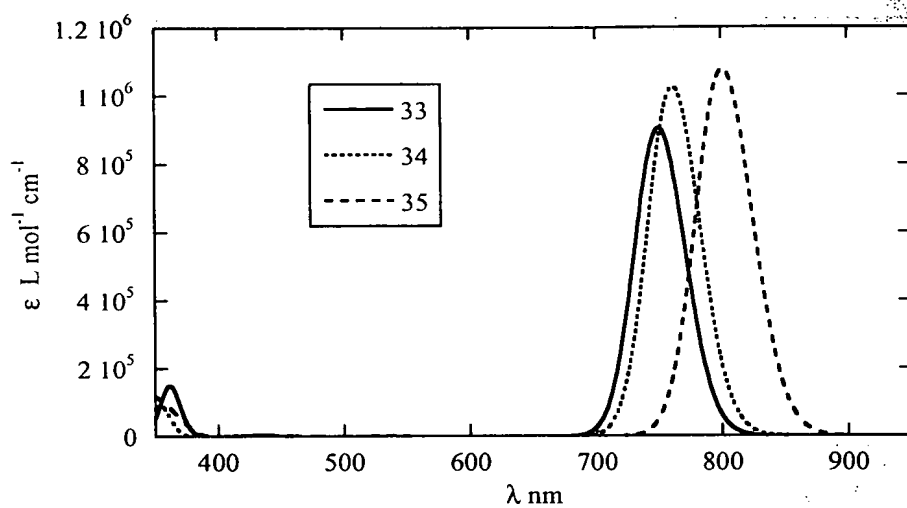


Figure 6A: Calculated absorption spectra for Formula 1 dyes as function of A (=B).

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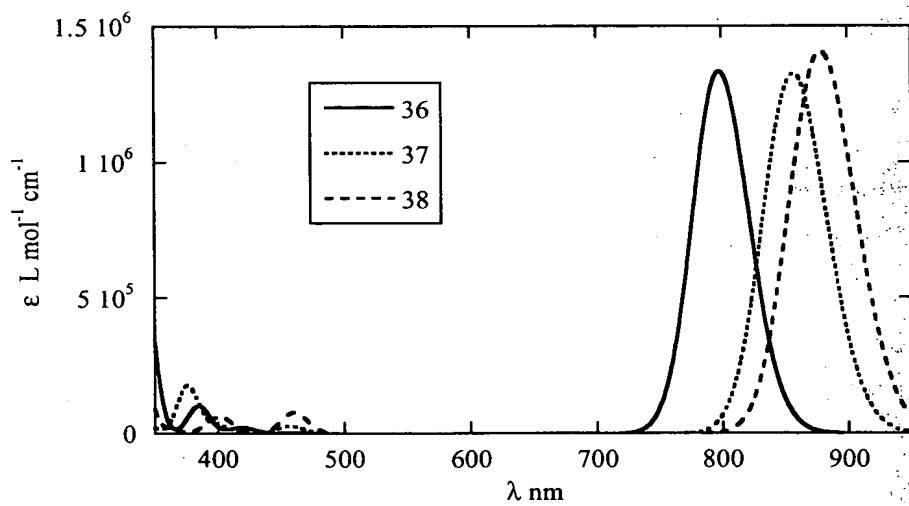


Figure 6B: Calculated absorption spectra for Formula 1 dyes as function of A (=B).

10

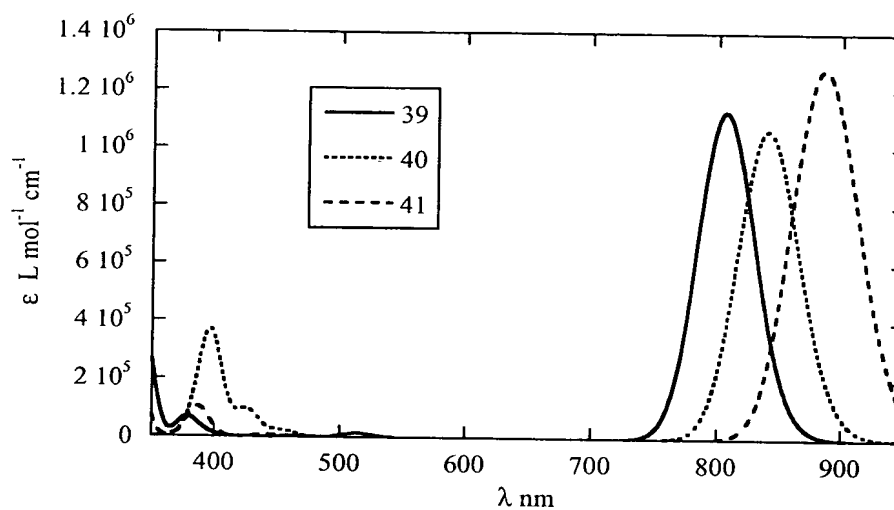


Figure 6C: Calculated absorption spectra for Formula 1 dyes as function of A
5 (=B).

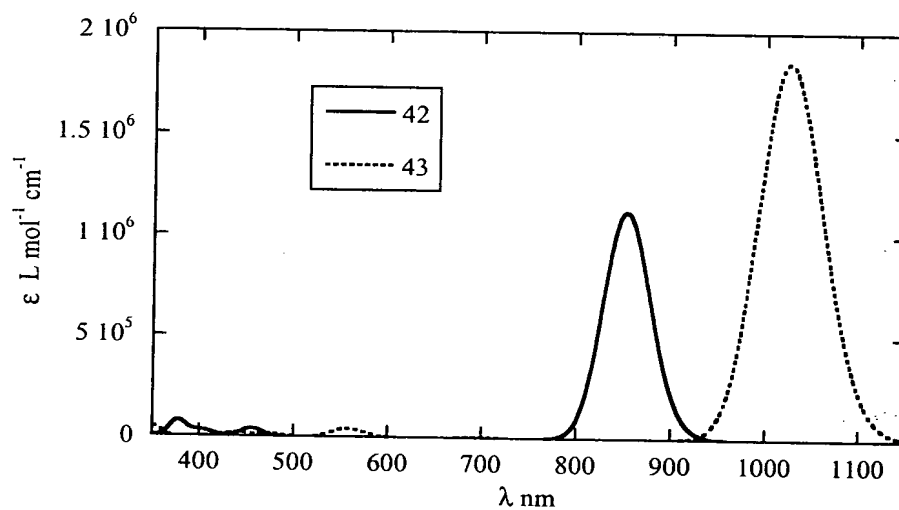


Figure 6D: Calculated absorption spectra for Formula 1 dyes as function of A
10 (=B).

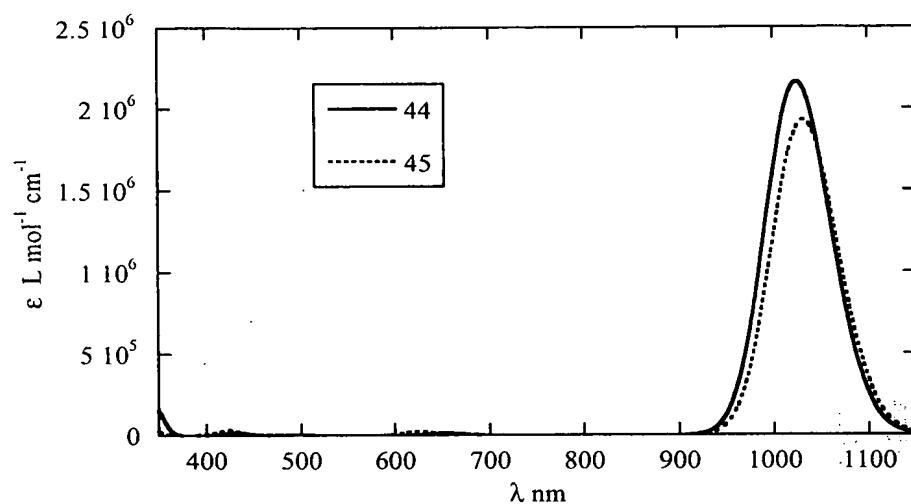


Figure 6E: Calculated absorption spectra for Formula 1 dyes as function of A (=B).

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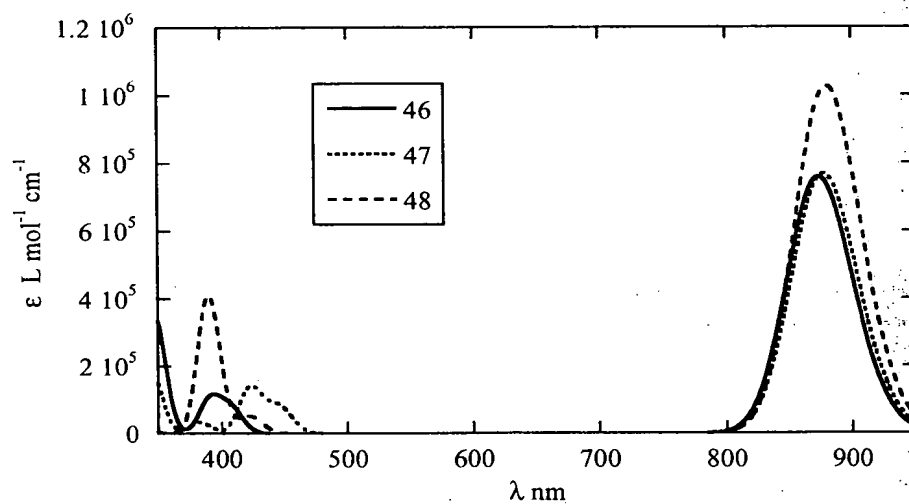


Figure 7A: Calculated absorption spectra for Formula 2 dyes as function of A (=B).

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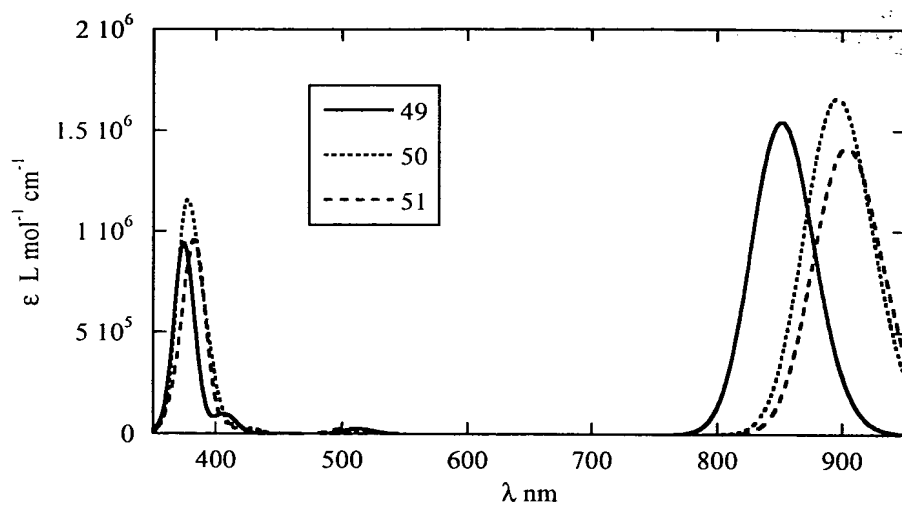


Figure 7B: Calculated absorption spectra for Formula 2 dyes as function of A (=B).

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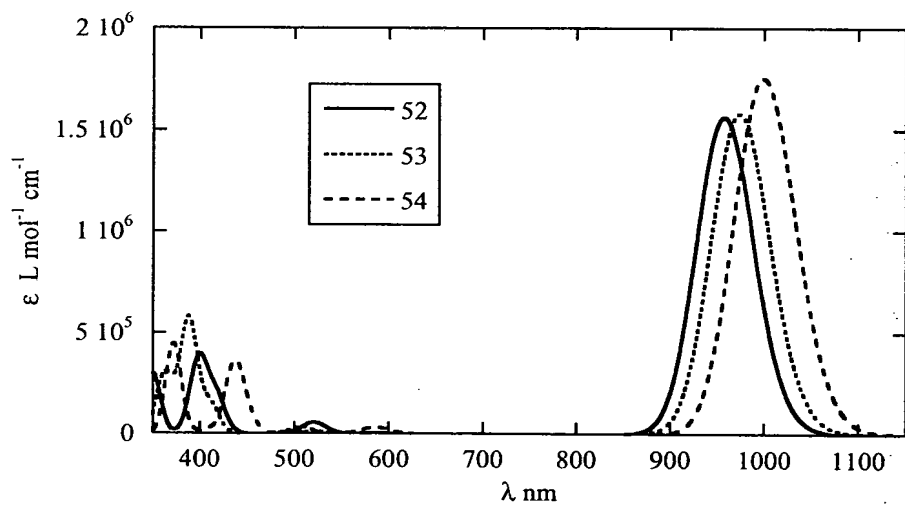


Figure 7C: Calculated absorption spectra for Formula 2 dyes as function of A (=B).

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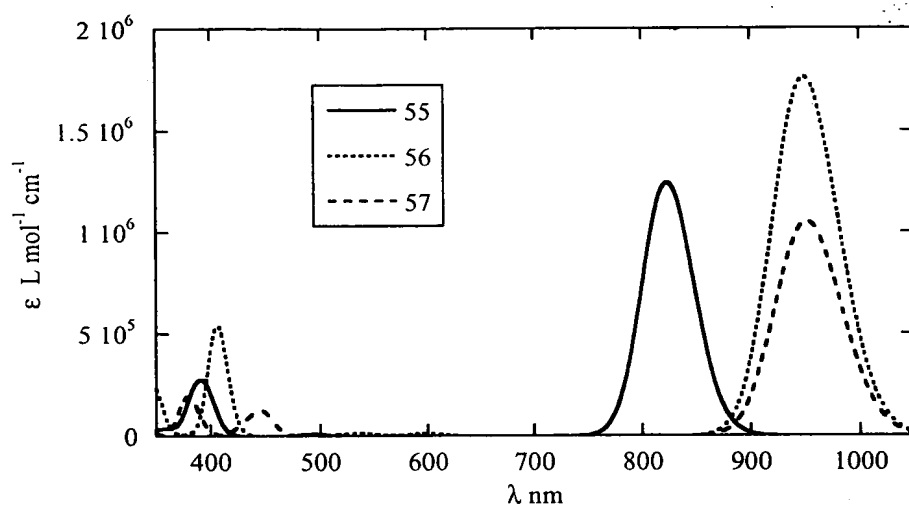


Figure 7D: Calculated absorption spectra for Formula 2 dyes as function of A (=B).

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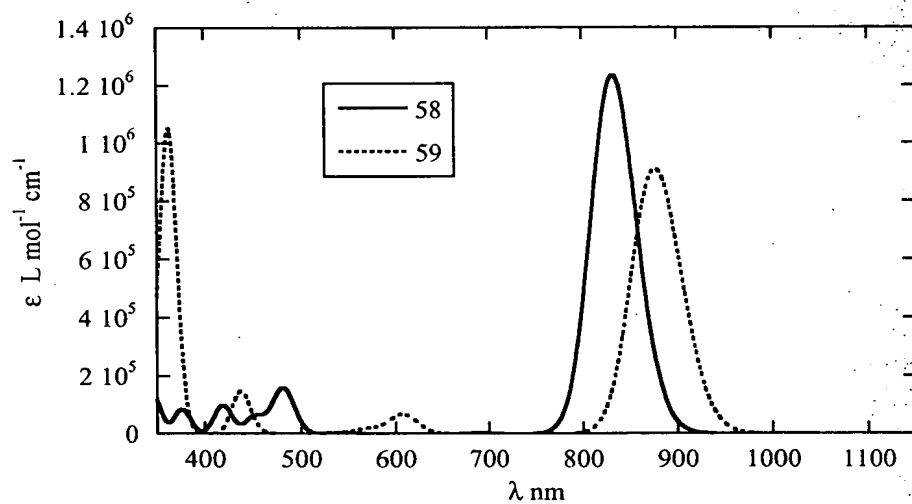


Figure 7E: Calculated absorption spectra for Formula 2 dyes as function of A (=B).

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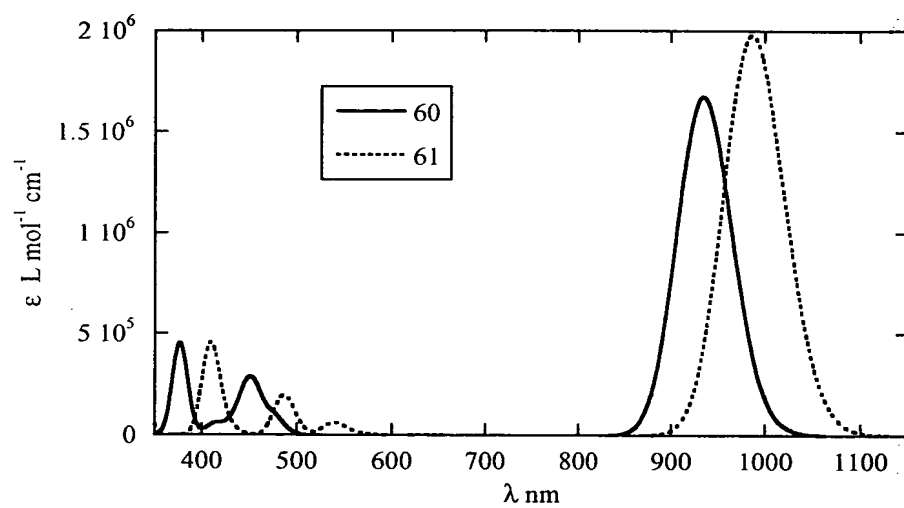


Figure 7F: Calculated absorption spectra for Formula **2** dyes as function of A (=B).